CONJUGATE ADDITION REACTIONS OF SORBOMESITYLENE AND SORBODURENE

BY

WILLIAM HARRIS LIBBY

A.B., Carleton College, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

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Introduction

Recent research has indicated that the benzyl and *t*-butyl groups alkylate benzoyldurene in the *para* position when this compound is treated with the corresponding Grignard reagents (1). Other alkyl groups of relatively low electronegativity also are known to undergo remote addition to the same and related ketone molecules (2). Because of this evidence a re-examination of the addition reactions of a doubly-conjugated acyclic carbonyl system was undertaken.

Sorbomesitylene and sorbodurene, the basic ketones used in this investigation, were selected to fulfill certain structural requirements. These molecules include the long conjugated system necessary for a study of the competition between the 4- and 6-positions in Grignard addition as well as a highly hindered carbonyl function incapable of being involved in carbinol formation. Grignard reagents were chosen for this comparative study on the basis of evidence garnered from the corresponding reactions of cyclic conjugated systems.

Discussion Of Results

The new doubly-conjugated ketones, sorbomesitylene and sorbodurene, were synthesized in suprisingly good yields from the acid chloride of sorbic acid, mesitylene or durene and anhydrous aluminum chloride by the method of Friedel and Crafts. In proving the structures of these compounds, the opportunity was seized to investigate their application as dienes in the Diels-Alder reaction. Both sorbomesitylene and sorbodurene have been found to condense with maleic anhydride to produce the substituted cyclohexenes.

Sorbomesitylene has been found to react with phenyl-

magnesium bromide in a 1,4-manner. The phenyl, benzyl and *s*-butyl Grignard reagents add to sorbodurene in a similar manner. Oxidative degradation with neutral potassium permanganate was employed to elucidate the structures of the Grignard adducts. The resulting crystalline, water-insoluble acids were characterized by analyses and neutralization equivalents, while the acetic acid produced by the oxidation was identified by conversion to the *p*-bromophenacyl ester.

This investigation lends support to the theory that Grignard reagents add to a doubly-conjugated carbonyl system in a 1,4-manner only. It has been shown that the nature of the organomagnesium compound itself is not a factor of importance in determining the mode of Grignard addition to an unsaturated acyclic ketone. This, then, leads to the supposition that the conjugate addition of Grignard reagents to cyclic and acyclic carbonyl systems must proceed by different routes.

The reaction of benzene with sorbomesitylene in the presence of aluminum chloride produces a mono- and diphenylated adduct. The former was not identical with a sample of β-phenyl-β-propenylpropiomesitylene prepared by the Grignard reaction.

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VITA

The author was born in Winona, Minnesota on January 25, 1922. He attended grade school in that town and was graduated from Winona Senior High School in June, 1940. In the fall of that year he entered Carleton College at Northfield, Minnesota where he remained until being called into the service in February, 1943. After serving two and one-half years in the Army Air Forces he returned to Carleton to complete his undergraduate work. Immediately after receiving the degree of Bachelor of Arts in June, 1946, he entered the Graduate School of the University of Illinois. He held a teaching assistantship from September, 1946, until August, 1948, and a University of Illinois Fellowship during the academic year of 1948-1949.

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